

Deactivation Mechanisms of SCR Catalysts During the Co-Combustion of Bio-Residues

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Summary

Concerning a reduction of the CO₂ emissions the substitution of fossil fuels by bio-residues such as sewage sludge, waste wood or meat and bone meal is of increasing interest. During the co-combustion of these fuel mixes in existing coal fired power plants an increased deactivation of SCR-DeNO_x catalysts is observed.

Analyses of deactivated catalyst samples indicate that the high concentration of phosphorus and sodium compounds as constituents of bio-residues has a significant influence on the deactivation rate. To determine the effect of these compounds, lab-scale experiments were carried out using doped synthetic flue gas. In bench scale tests the behaviour of phosphorus was investigated during the combustion of coal and phosphorus rich secondary fuel. Analyses of PRB coal indicate the presence of organically bound alkali and phosphorus species. The fuel concentration of both compounds is comparable to those of fuel mixes in European plants. In operation, possibly similar effects can be observed.

Effect of Phosphorus on Catalyst deactivation

Recent operational experiences showed that in case of meat and bone meal (MBM) co-combustion in German utilities a share of 4 wt-% MBM leads already to a severe deactivation of the installed SCR-catalyst. Phosphorus and alkali compounds in the fuel are considered as primary deactivating elements. The approximate concentration of P in the fuel in this case is 0,4 wt-%, the content of alkalis 0,1 wt-%.

Concerning sewage sludge co-combustion of 4 wt-%, the P share in the fuel is 0,25 wt-% which also leads to a considerable deactivation. These results were confirmed by the analysis of full scale catalyst samples exposed to co-combustion. Analyses of PRB coal give a high share of organically bound alkalis as well as P bound as phosphate with some organic share of 10 %. These results are similar to MBM with alkali compounds as well as calcium phosphate and some share of organically bound P which are easily released during combustion. The experience of catalyst deactivation in Europe therefore may be transferred to the combustion of PRB coal where similar effects are likely.

Combustion Tests

Combustion tests with pure hard coal and a mixture of 5% sewage sludge and lignite are carried out in a 500 kW pulverised-coal facility. Particulates and gaseous P samples are collected at 900, 600 and 300 °C. The fly ash and particulate matter is analysed by XRF. For the estimation of the P concentrations in the solutions photometry was applied.

Deactivation Tests

In order to obtain information on the effect of phosphorus on the SCR catalyst activity, deactivation tests are carried out in a fixed bed micro reactor in turbulent flow conditions using H_3PO_4 as phosphorus compound. Based on a fuel mix of 5 % of MBM or sewage sludge, the resulting gas concentration is about 500 ppm P_2O_5 . The flue gas composition is adjusted to 4,5 % O_2 , 5 % H_2O , 450 ppm SO_2 and 600 ppm NO in N_2 . In the test series the catalyst is conditioned for 4 h with SO_2 ; the H_3PO_4 concentration is varied from 0 to approximately 1500 ppm. A reference sample is exposed for 8 h to SO_2 only. The activity is estimated before and after deactivation in laminar flow conditions by measuring the NO reduction potential. From the inlet and outlet NO concentration the relative activity of the catalyst k/k_0 is determined.

Results

BET surface analysis, XRF analysis of the bulk material as well as SEM/EDX investigations on the surface composition are carried out. After exposure to H_3PO_4 a significant decrease of the relative activity can be observed. The decrease occurs at moderate concentrations of 500 ppm already. The BET surface area as well as the average pore diameter or the total pore volume showed no significant change. XRF analysis of the bulk material showed no relation to k/k_0 . To get information on the surface composition a SEM/EDX analysis was carried out at the reference sample and the sample exposed to the highest phosphorus concentration. The comparison of the element mapping showed a clear qualitative difference in the P load.

The results of the combustion tests indicate a higher phosphorus flue gas concentration with a peak at 600 °C for sewage sludge co-combustion. The maximum concentration of PO_4^{3-} however was only 0,02 $\mu\text{g}/\text{Nm}^3$ at 600 °C.

Discussion and Conclusion

The results of the deactivation tests indicate dependence between phosphorus load in the flue gas and catalyst deactivation. The analysis of the P-species in the flue gas showed a higher concentration of PO_4^{3-} compared to the reference flame. However, the absolute flue gas concentration is below the estimated value. Reason is seen in the condensation behaviour of phosphorus, which primarily condensates as polymeric pyro- or polyphosphates which are difficult to analyse. The assumption for the deactivation experiments is the formation of H_3PO_4 in the flue gas. The presence of PO_4^{3-} was confirmed in the combustion tests.

The nature of the deactivation mechanism as well as the formation of P-compounds during the combustion is not clarified. It is assumed that condensed P-compounds create a surface layer, which is indicated by the XRF and the EDX results.

In order to obtain more information on deactivation mechanisms, the release of P as well as its condensation along the flue gas path has to be analysed in detail by using appropriate methods for the estimate of polymeric phosphate species. This will create a basis for detailed equilibrium calculations in order to derive condensation behaviour or possible chemical reactions on the catalyst.

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